Welcome to

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Chemical Reaction Kinetics at the Academic-Industrial Interface

L.W. Bolton, L.A. Chewter, F. Galimberti, J.J. Heiszwolf, X. Nijhuis, H. Spohr, E.H. Stitt, R. van Duren, **J.J. Verstraete**, P. Wenmakers, H-J. Zander

Origin of the EUROKIN Consortium

- Use of Kinetics in Industry
  - 1995 Industrial Survey
    - Initiative of EFCE Working Party – CEAC
      - organised by 1 university lab (University of Eindhoven) and 3 companies (Dow, DSM, Shell)
    - Questionnaire sent out to 37 companies
    - Response from 24 companies
      - Chemicals, Oil, Catalysts, Engineering
    - Report prepared 1Q 1996
      - published in abbreviated form in 1997 [1]

- Some learnings …

[1] Bos ANR, Lefferts L, Marin GB & Steijns MHGM, Applied Catalysis A: General, 160, 185-190 (1997)

Utilisation of Kinetic Data in Industry: Overall [2]

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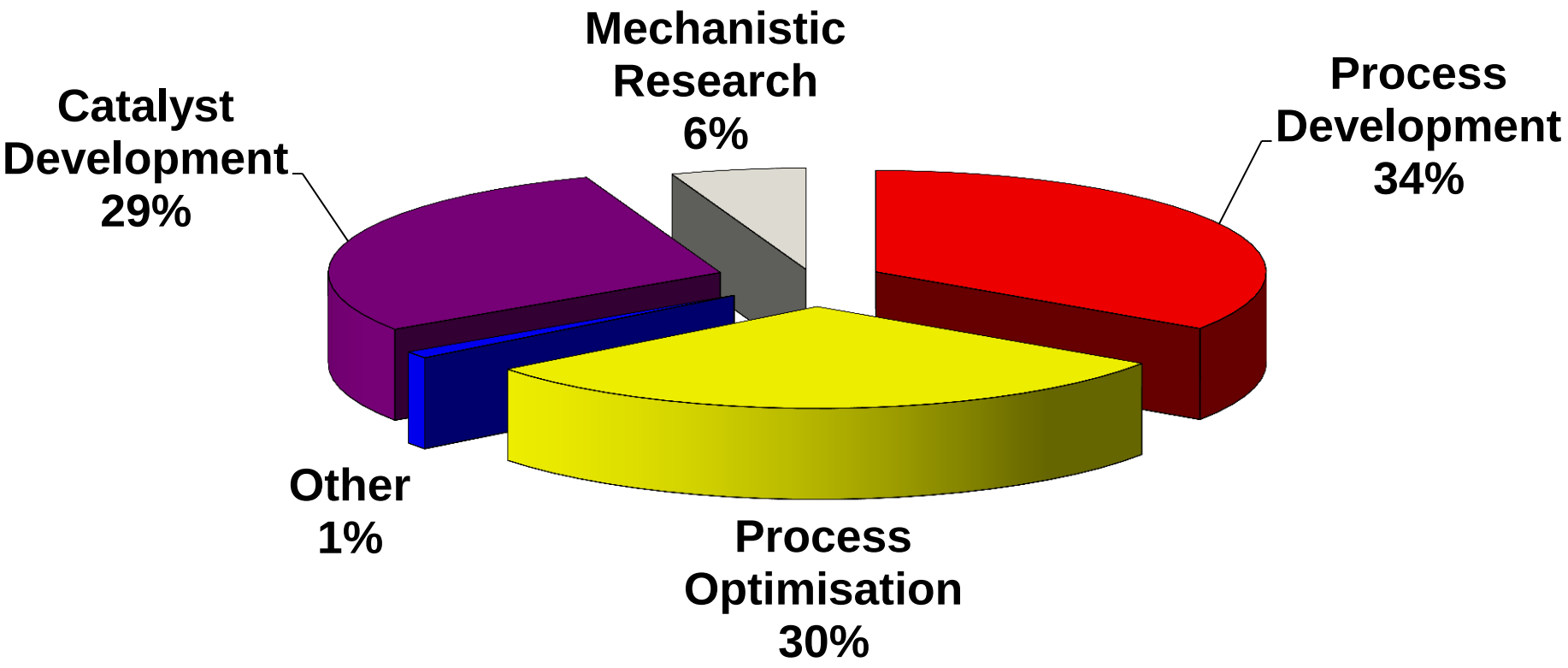
- Utilisation of kinetics:
  - 1/3 Process Development
  - 1/3 Catalyst Development
  - 1/3 Process Optimisation



[2] Berger RJ, Stitt EH, Marin GB, Kapteijn F & Moulijn JA, CatTech, 4 (2) 30-60 (2001)

Utilisation of Kinetic Data in Industry: Different Industry Sectors [2]

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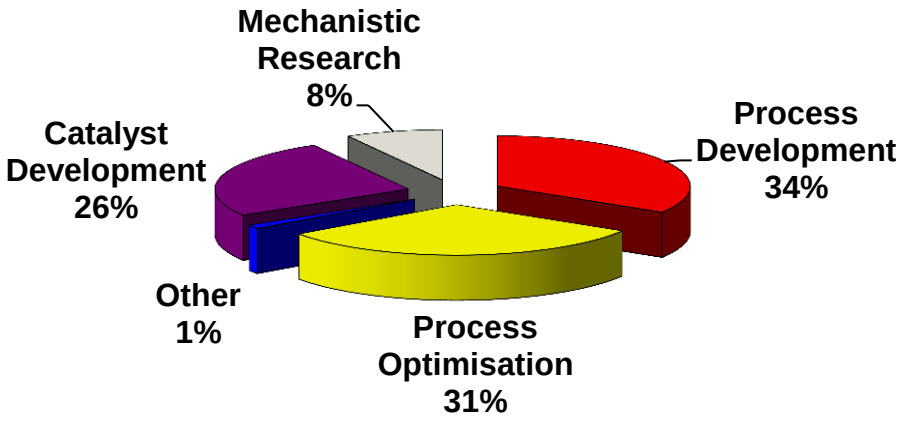
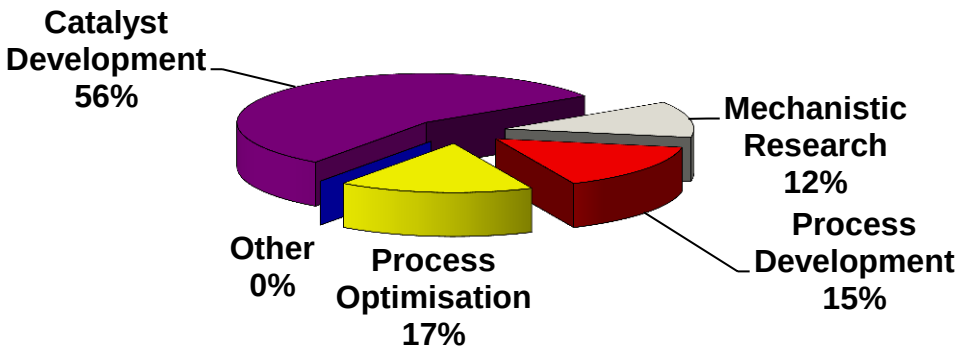
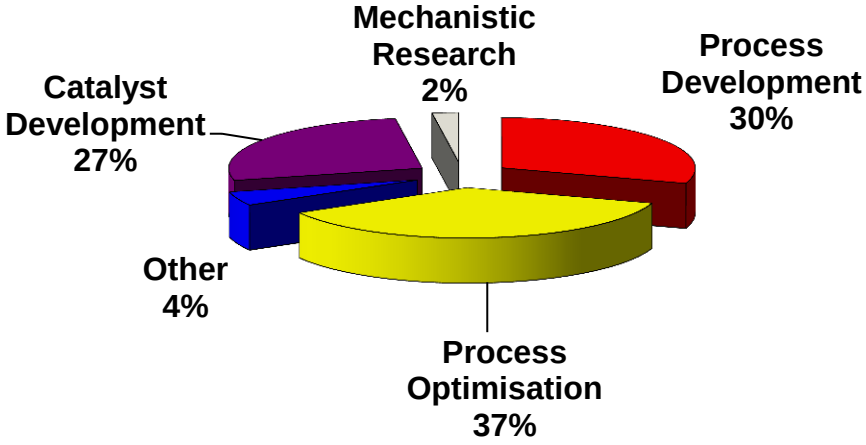
Chemical Companies



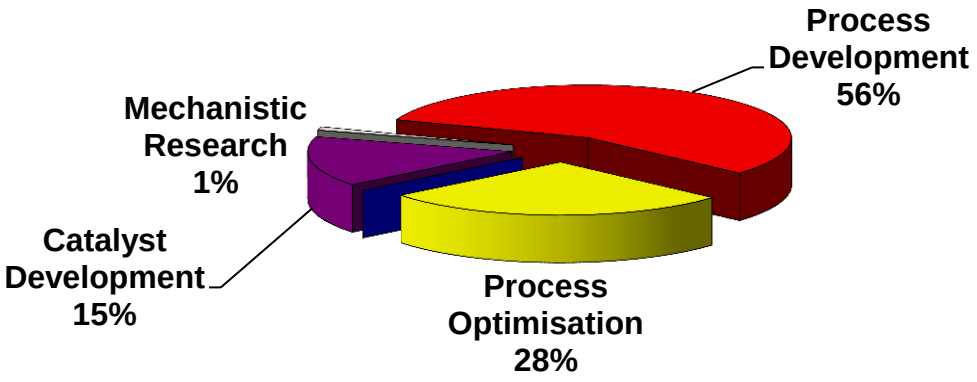
Catalyst Companies



Oil Companies



Engineering Companies



[2] Berger RJ, Stitt EH, Marin GB, Kapteijn F & Moulijn JA, CatTech, 4 (2) 30-60 (2001)

Acquisition of Kinetic Data in Industry

- Experimental Approaches
  - Use of pilot plants
    - All respondents (except one) use in-house tests
    - All use fixed bed meso- or micro-reactors
      - Only 25% cite gradientless reactors
      - Temperature programmed techniques cited only by 3 (12%)
      - One cites the use of a TAP reactor
  - Other data sources
    - 40% cite use of external data
    - [Only] 20% cite use of plant data

Acquisition of Kinetic Data in Industry

- Experimental Approaches
  - We may not always be as careful as we ought to be
    - Plug flow commonly assumed
      - but the separate study of hydrodynamics (using cold flow models) is rare
    - Isothermicity is not always ensured
      - even when powdered catalyst is used
    - Use of appropriate (micro)-reactor models for data interpretation is not widespread
  - Engineering companies appear to favour intrinsic kinetics the most, while catalyst companies use them the least

Why Do We Need Intrinsic Reaction Kinetics?

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- Major advantage
  - Intrinsic reaction kinetics is **scale independent**, in contrast with often-used, so-called apparent kinetics
    - The influence of (disturbing) transport phenomena have to be separated from the chemical reactions

  Reliable intrinsic kinetic rate expressions are a prerequisite for safe and economical reactor design

- Drawbacks
  - cannot be found in literature
  - are system dependent (catalyst, operating conditions, …)
  - are not easy to measure

Conclusions from the Survey

- General feedback from industry
  - Experiments are **expensive** (time / resources)
  - There needs to be a **technical justification** for the model
  - There must be a **financial justification** for kinetic studies
  - When performed, kinetics studies in industry are **pragmatic**
    - Relatively old methods and techniques
    - Limited or even superficial data interpretation
  - Major usage is in process research
    - Process models do not need detailed kinetics

Benchmarking Industry vs. Academia

- Kinetic modelling approaches
  - **Model "non-complexity"** is generally preferred
    - Frequent lumping of transport and kinetics
    - Simple "order" or LHHW models predominate
    - Little or no significant use of mechanistic or ab initio models
  - The advantages of intrinsic kinetics are generally known and acknowledged …… but are not always considered to outweigh the difficulty in obtaining them
    - cost & man-hours
    - time
    - economic justification
    - technical justification

What is industry doing about it?

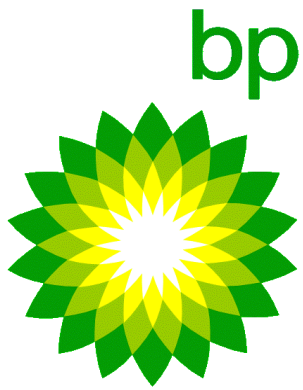
- **"Self help"** club: The EUROKIN Consortium
  - Created in 1998, celebrating its 20th anniversary !
  - 100% funded by member companies

- Aim
  - Implementation of best practices in the area of chemical reaction kinetics in an industrial environment
    - Competitive advantage through being good at experimentation, theory and modelling
  - Development of internal pre-competitive tools
    - Academic research to support these objectives

      ↪ Faster, cheaper, better reaction rate expressions, enabling faster development and more accurate designs

Who?

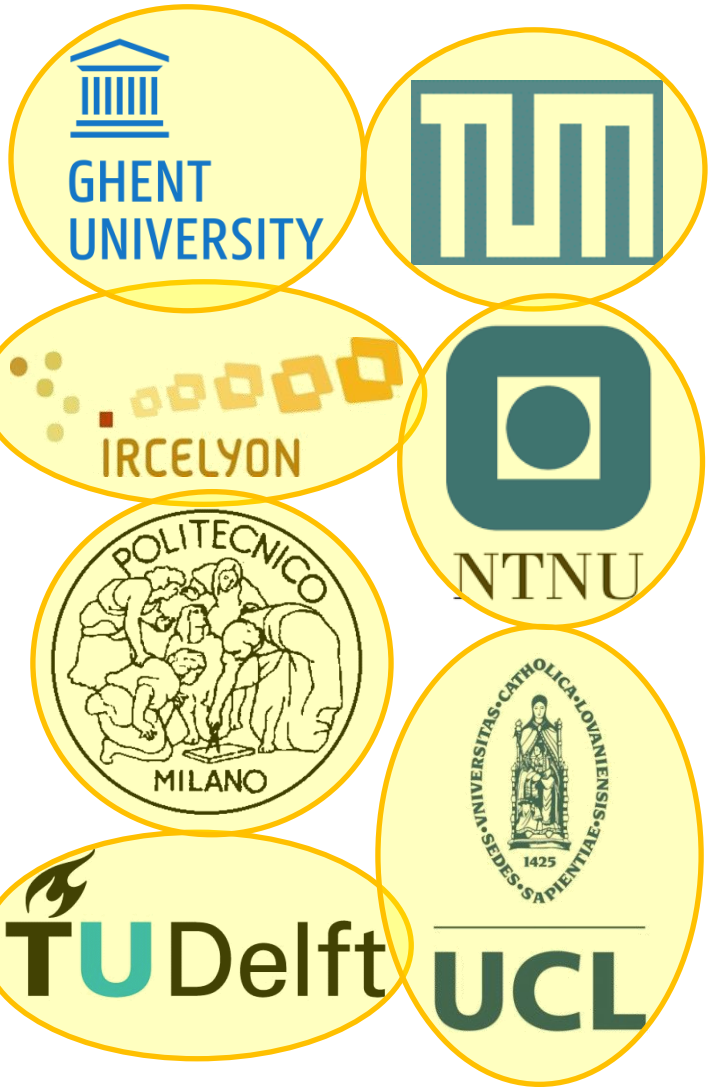
- Industrial members



Academic members

Who?

- Academic participants



National Technical University Athens

UNIVERSITY OF CAMBRIDGE

ICMSE (Sevilla)

Karlsruher Institut für Technologie

CPERI
Chemical Process and Energy Resources Institute

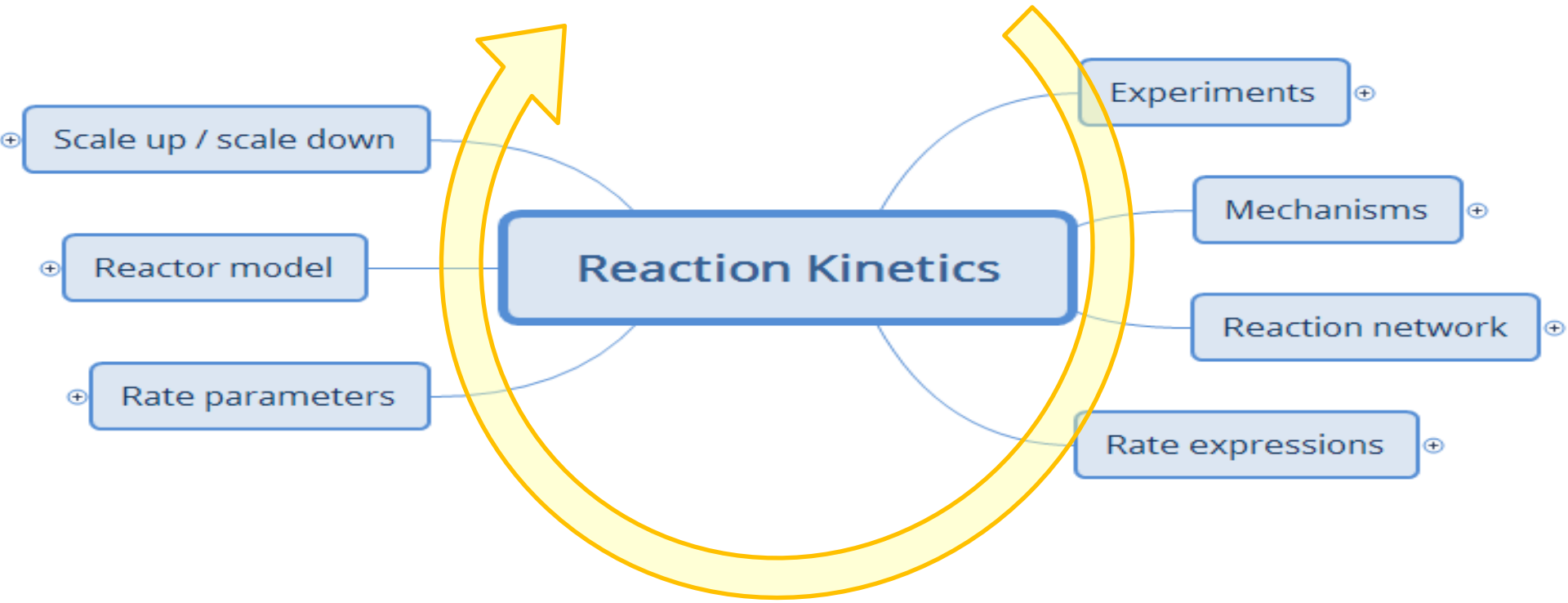
Who?

- Industrial members (between 7 and 12)
  - **Albemarle**, **BP Chemicals**, Dow Chemical, **DSM**, EC Chem Technologies, **ENI**, **Evonik Industries**, **IFPEN**, Ineos, **Johnson Matthey**, **Lhoist**, **Linde**, **SABIC**, Saudi Aramco, **Shell Chemicals**, StatoilHydro, Technip Benelux
- Academic participants
  - **Ghent University**, **TU Delft**, **Norwegian University of Science and Technology (NTNU)**, **Politecnico di Milano**, **Université Catholique de Louvain**, **IRCeLyon, TU Munich**
  - CPERI, LGPC, Northwestern University, Ohio State University, TU Eindhoven, University College of London, University of Cambridge, University of Edinburgh, …

Eurokin Consortium

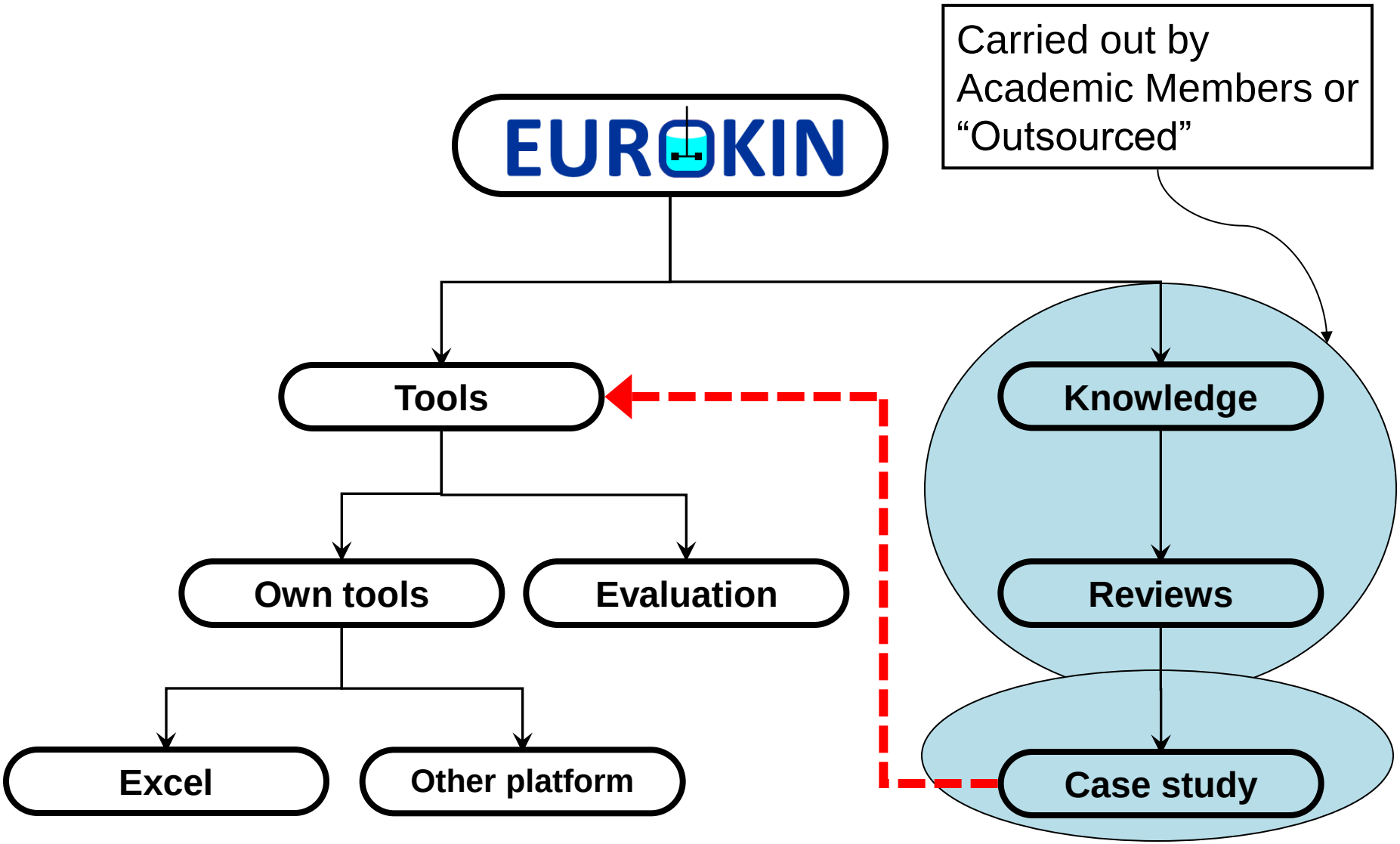
- Organisation
  - Programme
    - Rolling programme without fixed termination date
    - Programme is updated each year, and depends on the priorities of the industrial members
    - Academic members provide support and guidance in the development and execution of the programme
  - Other
    - 3 meetings per year (workshop + Main Committee meeting)
    - Industrial members pay yearly fee (currently € 12,500)
    - Confidentiality agreement concerning foreground and background information and knowledge
    - All members are allowed to use all tools and reviews

Typical work flow for kinetic studies



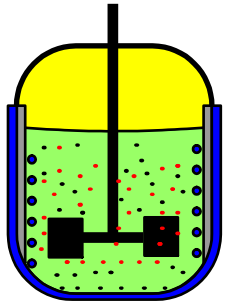
All these subjects are or have been covered by Eurokin investigations !

Eurokin 'Ways of Working'



What have we done up to now?

- (1) Experimental set-ups
  - Suppliers of reactor set-ups
  - Reactor selection for reaction kinetics experiments
  - Guides and software to assess experimental conditions for intrinsic kinetics
    - Fixed bed (including trickle bed), Fluidized bed, Slurry
    - Structured catalysts (e.g. monoliths, foams)
  - Adiabatic reactors and reactors for strongly exothermic reactions
  - Non-thermal reactors (plasma reactors, microwave)



What have we done up to now?

- (2) Kinetic data analysis
  - Kinetic parameter estimation methods and best practices
  - Comparison of software packages for kinetic parameter estimation
  - Sequential experimental design (advantages / tools)
  - Coping with irreducible transport phenomena
  - Dynamic methods (to obtain kinetic information)
  - Data reconciliation techniques

What have we done up to now?

- (3) Modelling
  - Non-experimental methods for estimating reaction rates
  - Reaction networks and lumping for complex systems
  - Liquid-phase reaction kinetics based on gas-phase experimental data (non-ideality, solvent effects)
  - Modelling catalyst decay and catalyst regeneration
  - Review of pore structure models
  - Extrapolation of models: perturbation analysis, error estimation
  - Coupling chemical kinetics with CFD
  - Phase (dis)appearance in GLS reactors
  - Limit cycle prediction during runaway

Some examples

- Example 1: Using meta-models
  - Can meta-models be used to provide sensitivity analyses (impact of inputs / parameters) ?
  - Can meta-models be used to identify where information lacks (sequential design) ?

- Example 2: Prediction of runaway conditions
  - Can the centre manifold theorem by used to analyse the bifurcation of a dynamical system ?

Illustration 1: Using meta-models

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- Meta-models
  - Why use a metamodel?
    - approximate the behaviour of the system if no model is available
    - provide a low-cost evaluation of a very complex model
- Can meta-models be used
  - to provide sensitivity analyses (impact of inputs / parameters)
  - to identify where information lacks (sequential design)

Illustration 1:
Using meta-models for sequential design

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- Collaboration with Lyon University
  - To give an overview of some meta-modelling techniques
  - To look at their possible application for
    - sensitivity analysis
    - sequential design

- Kriging
  - provides an estimate of uncertainty over the entire domain
  - can be used to perform sequential design in the absence of a model!

Illustration 1:
Using meta-models for sequential design

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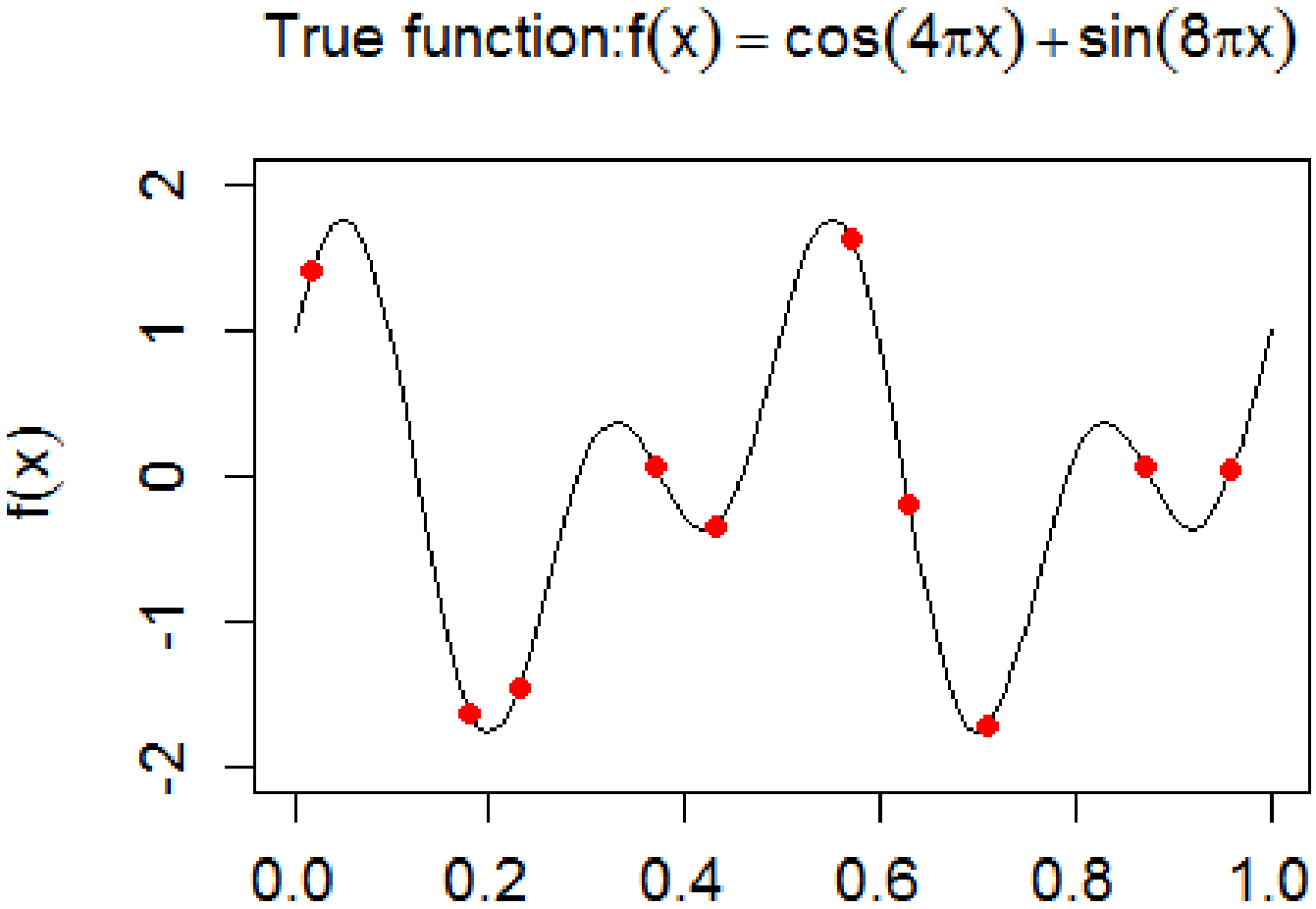
- A theoretical example



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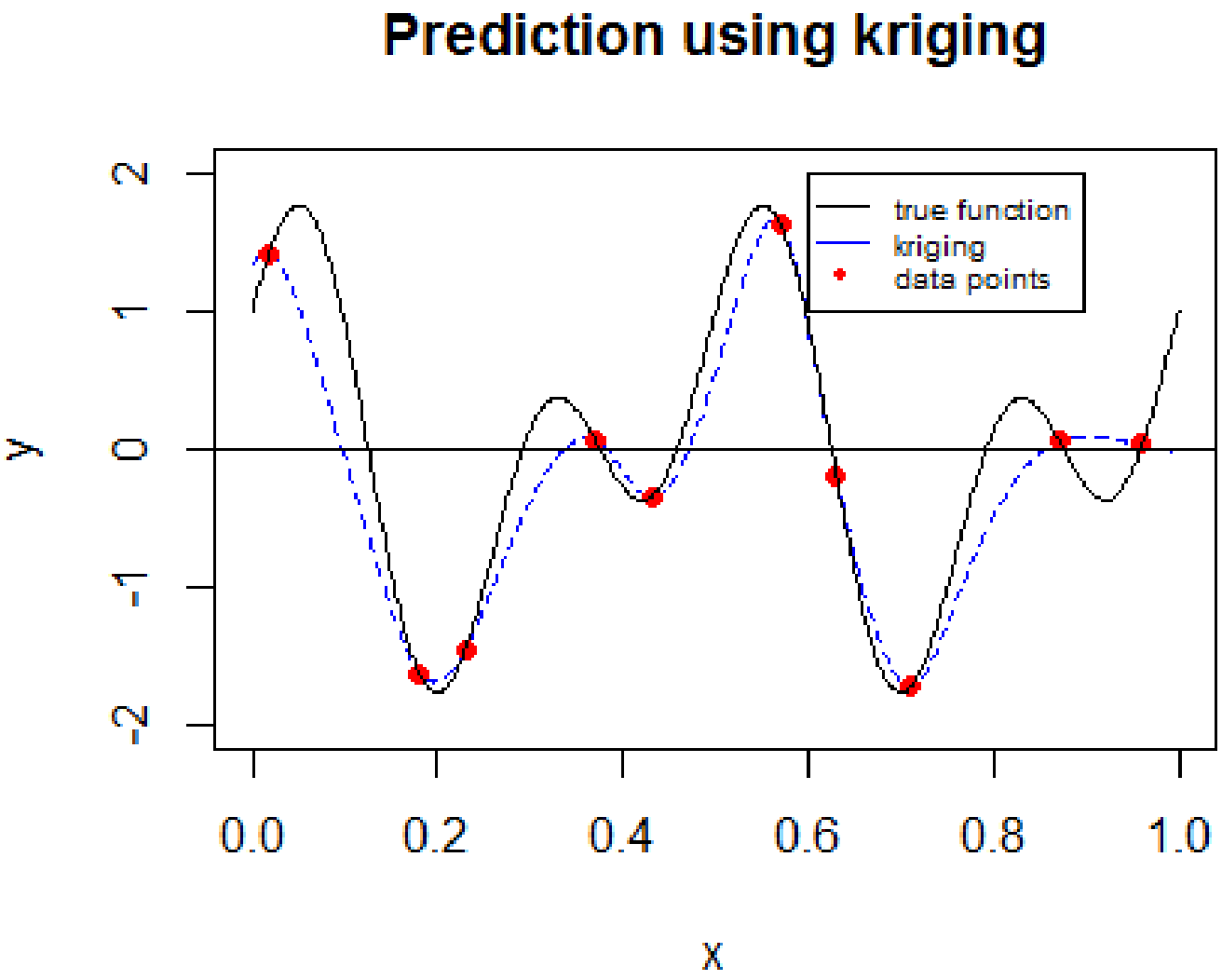

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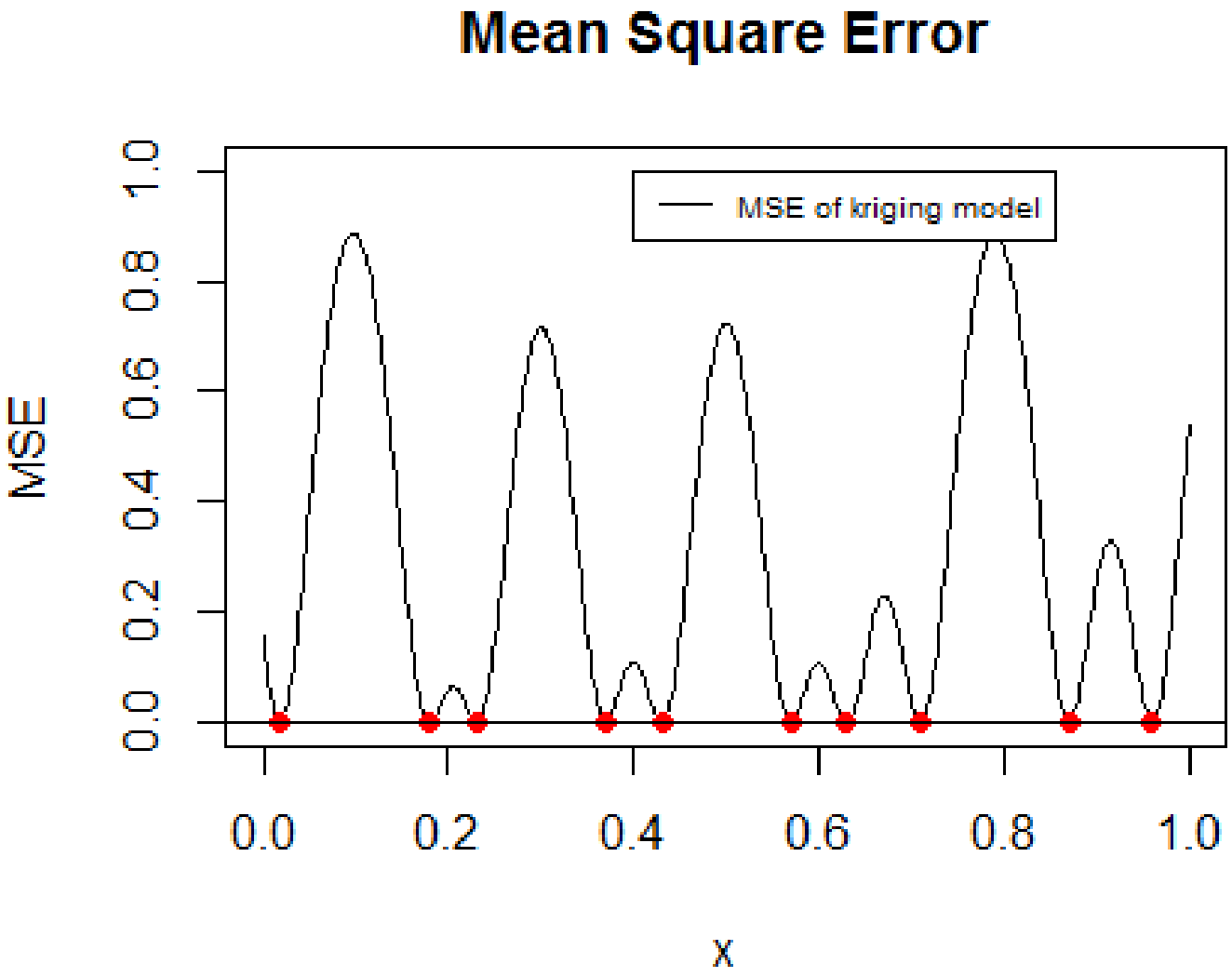

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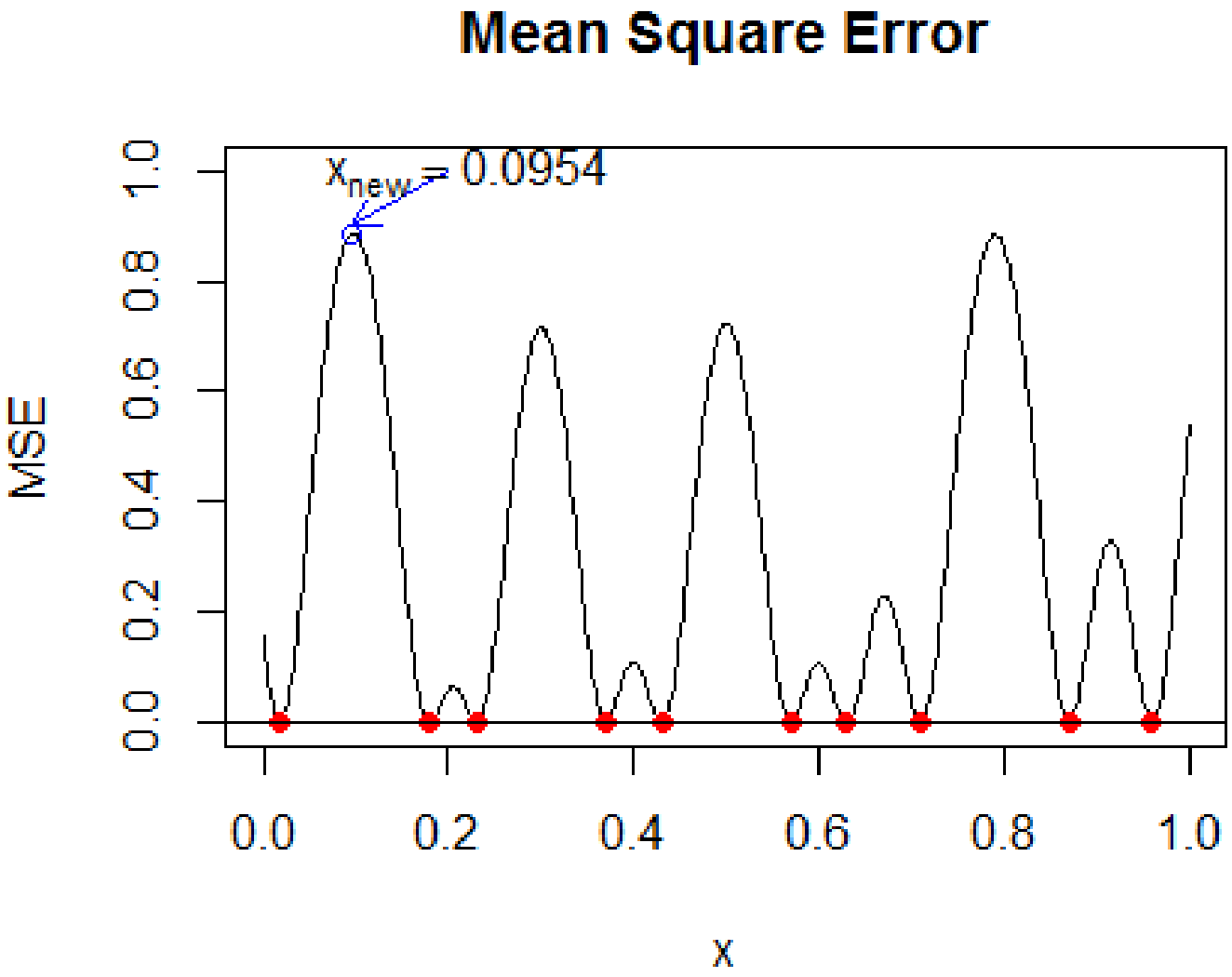

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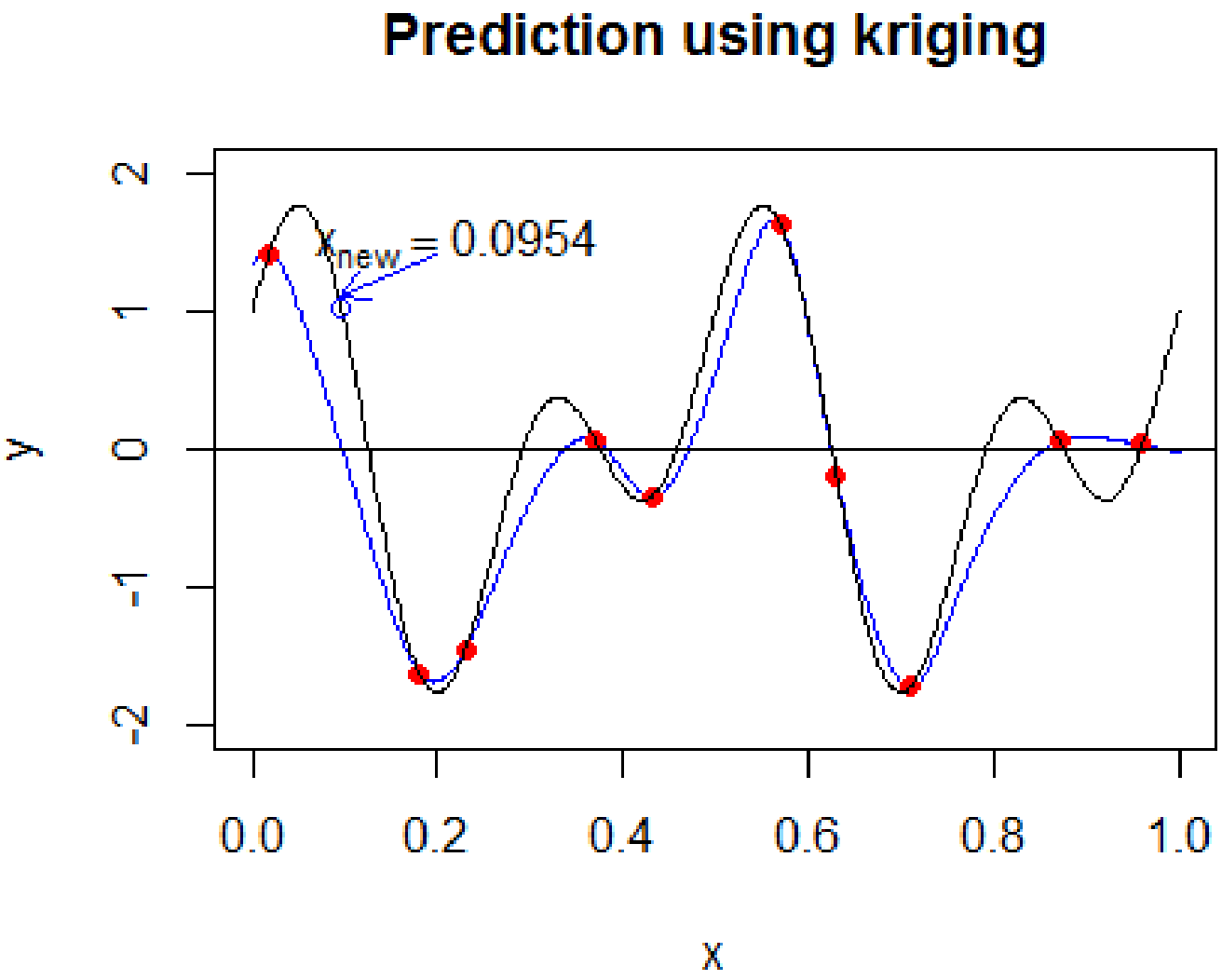

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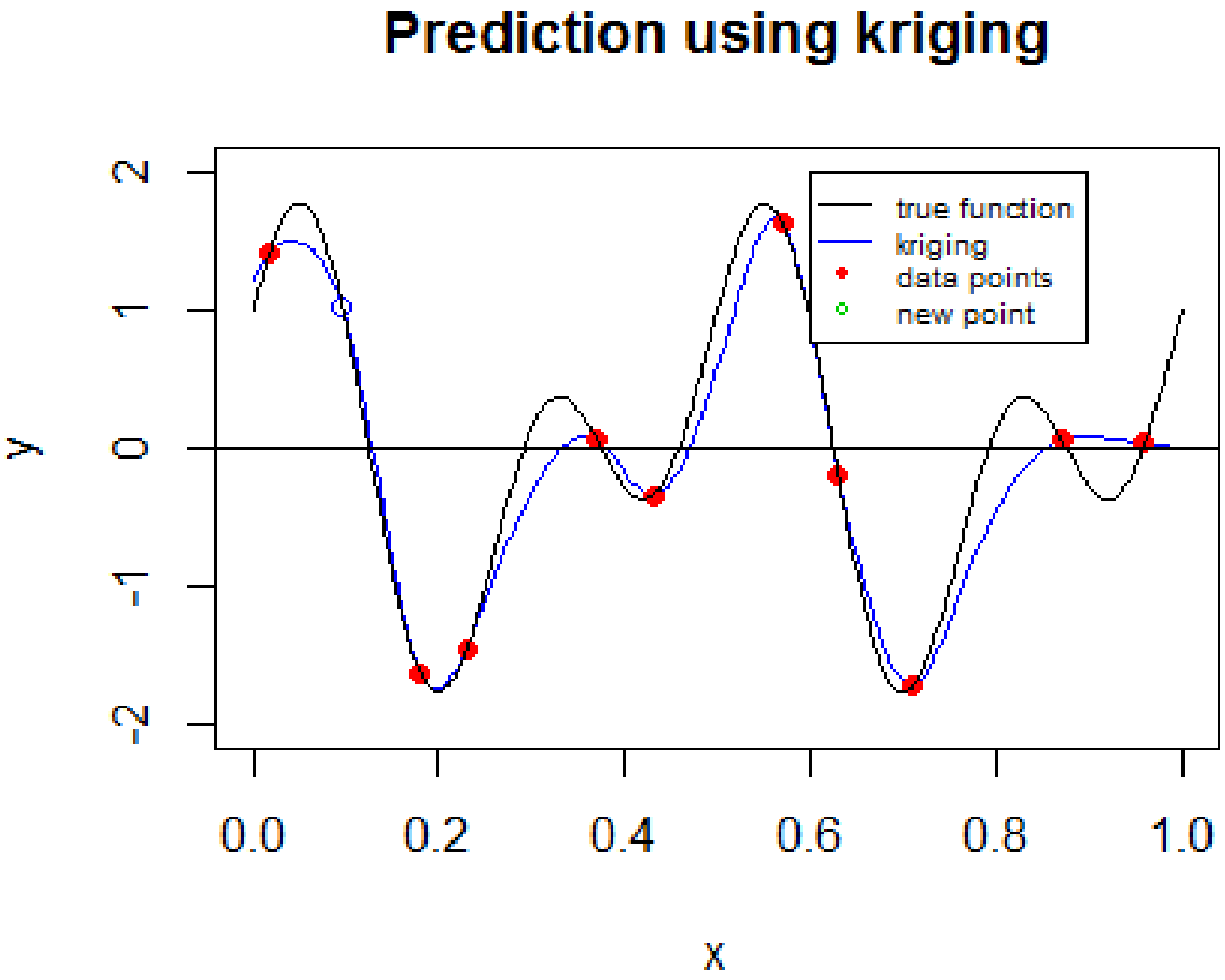

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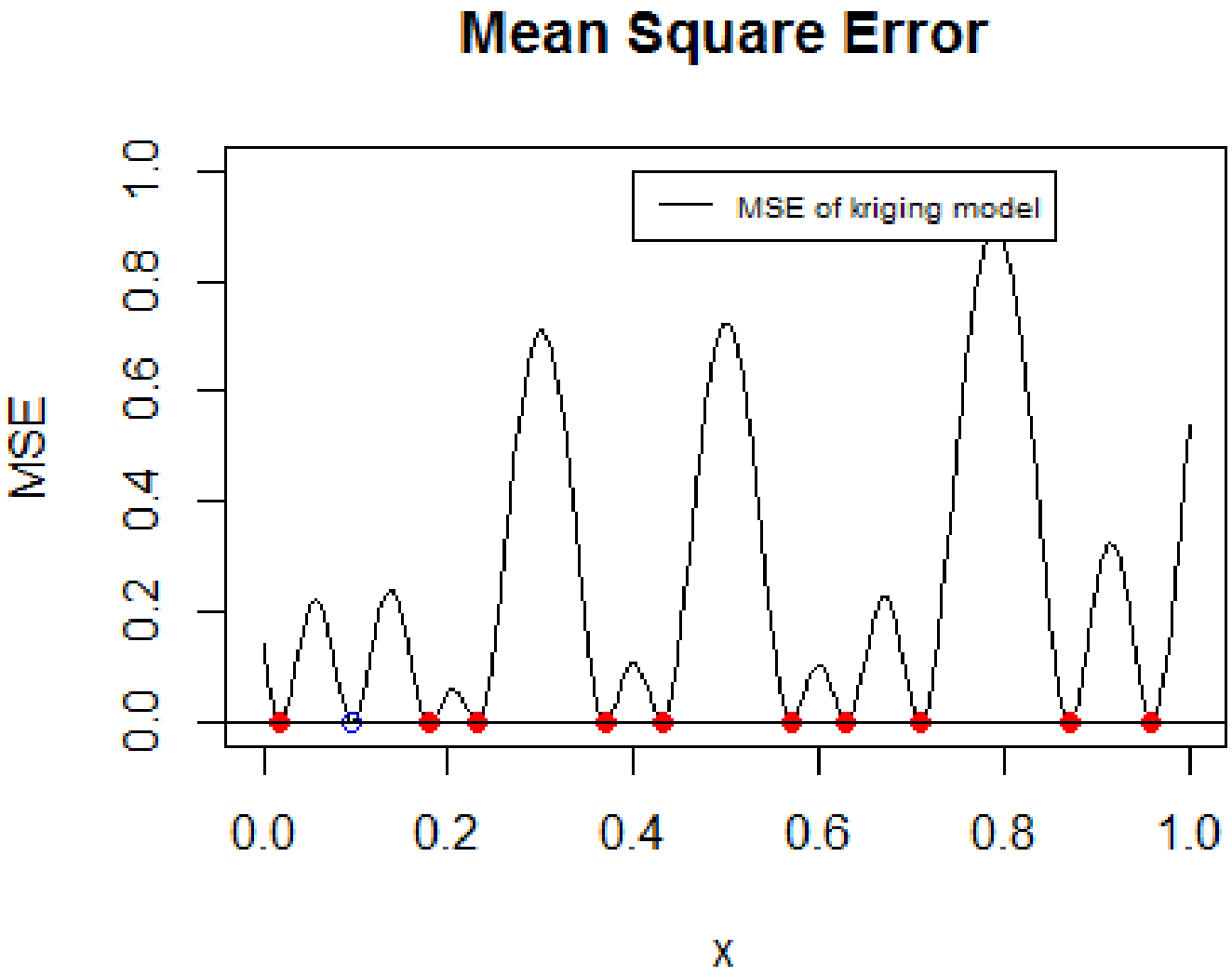

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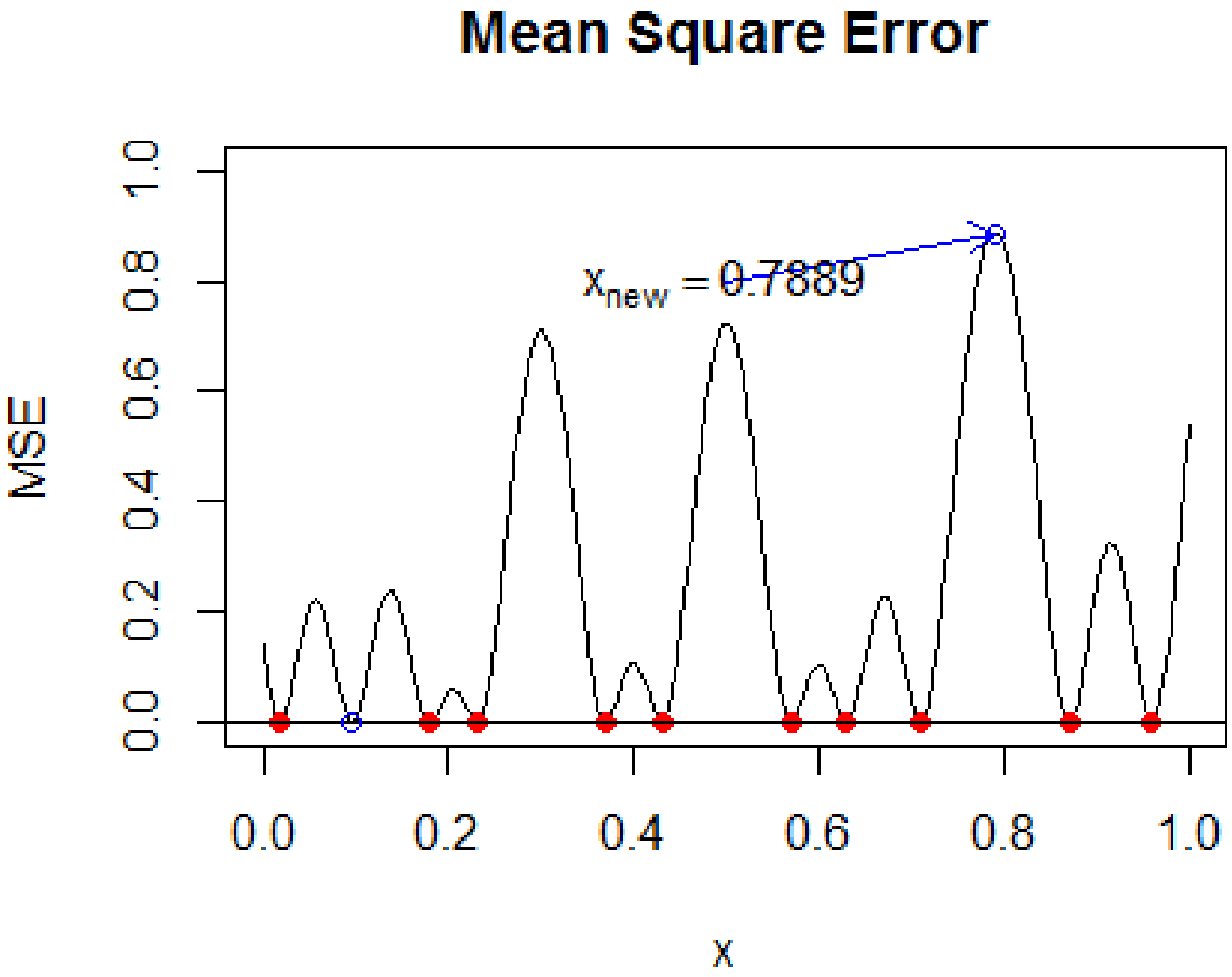

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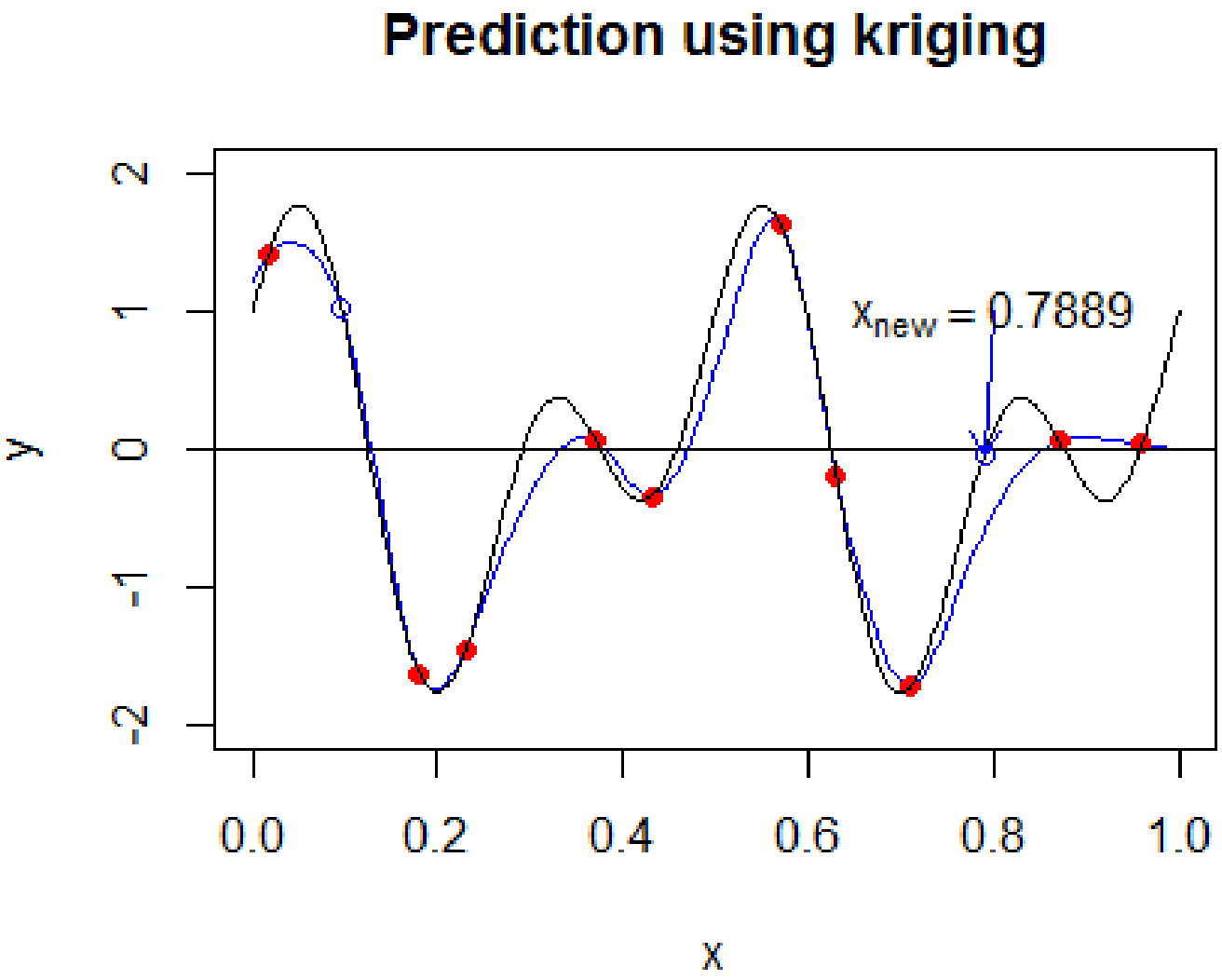

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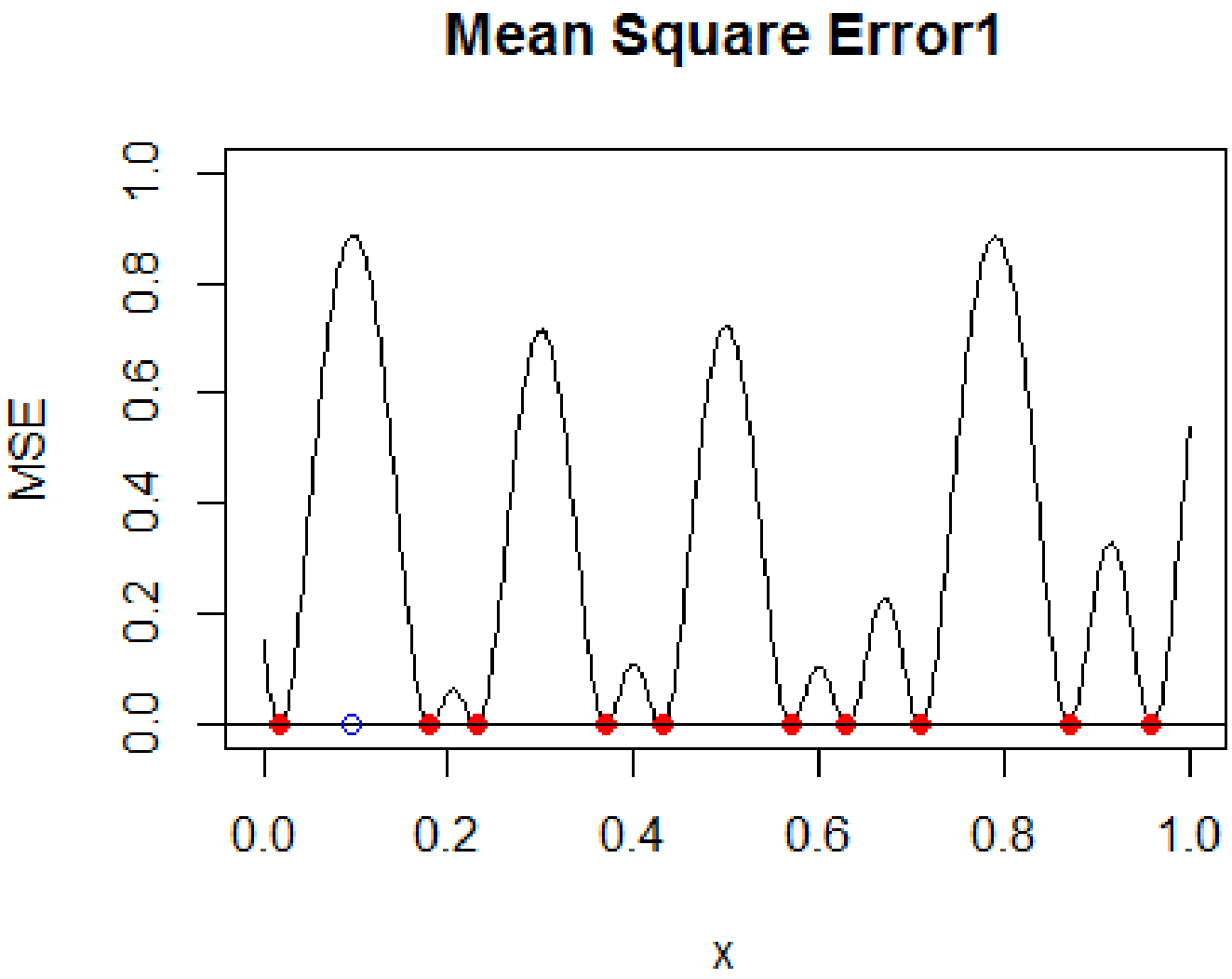

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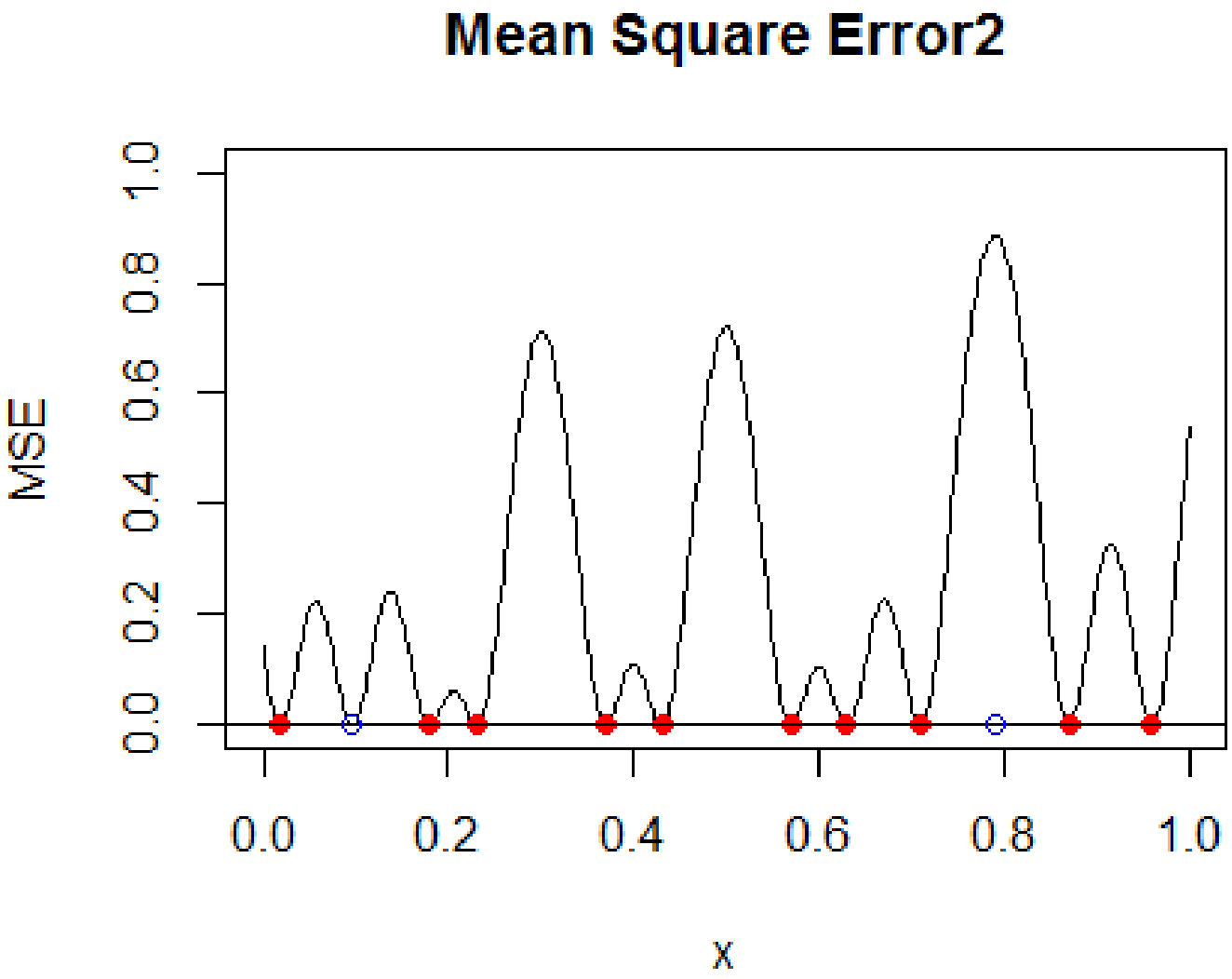

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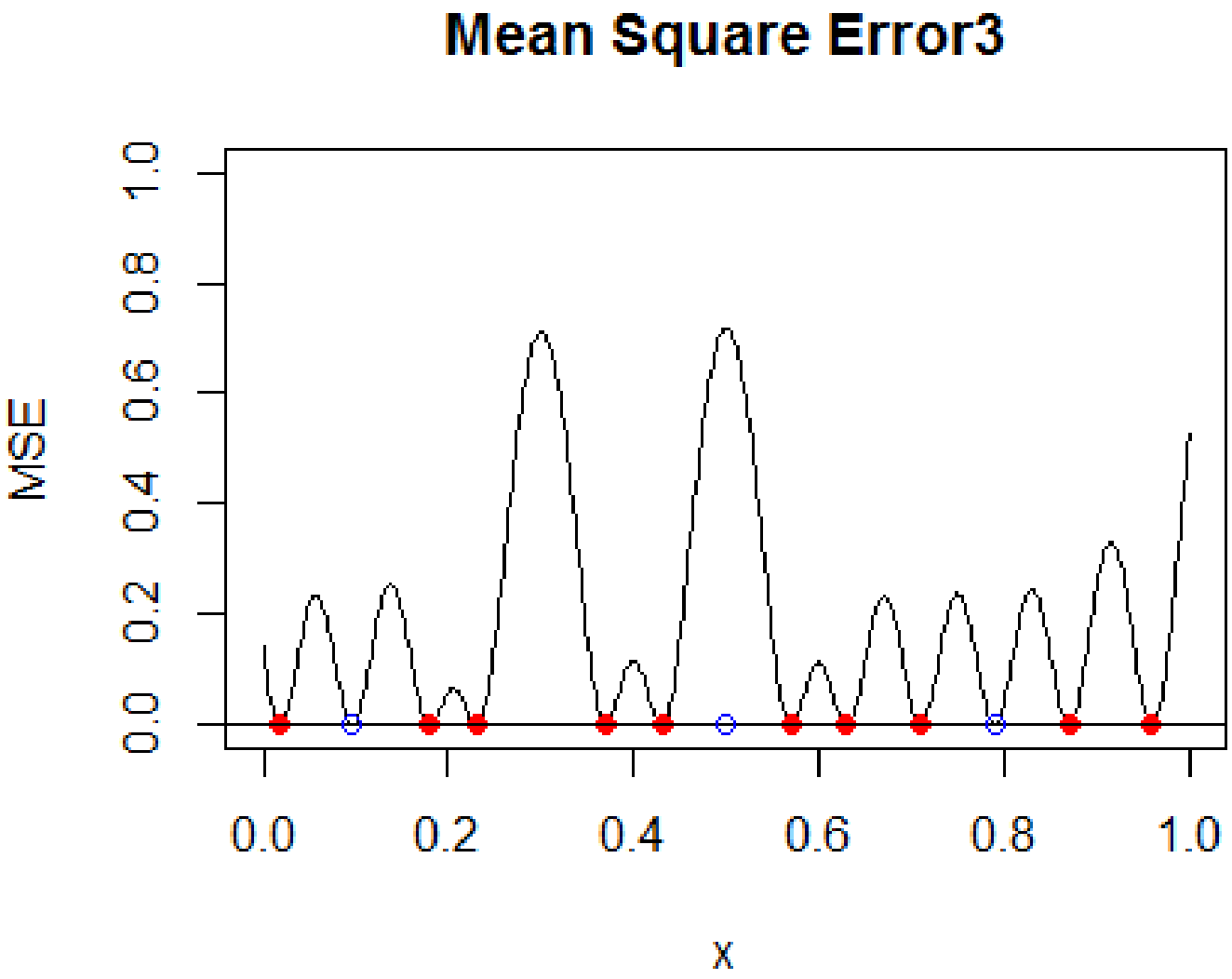

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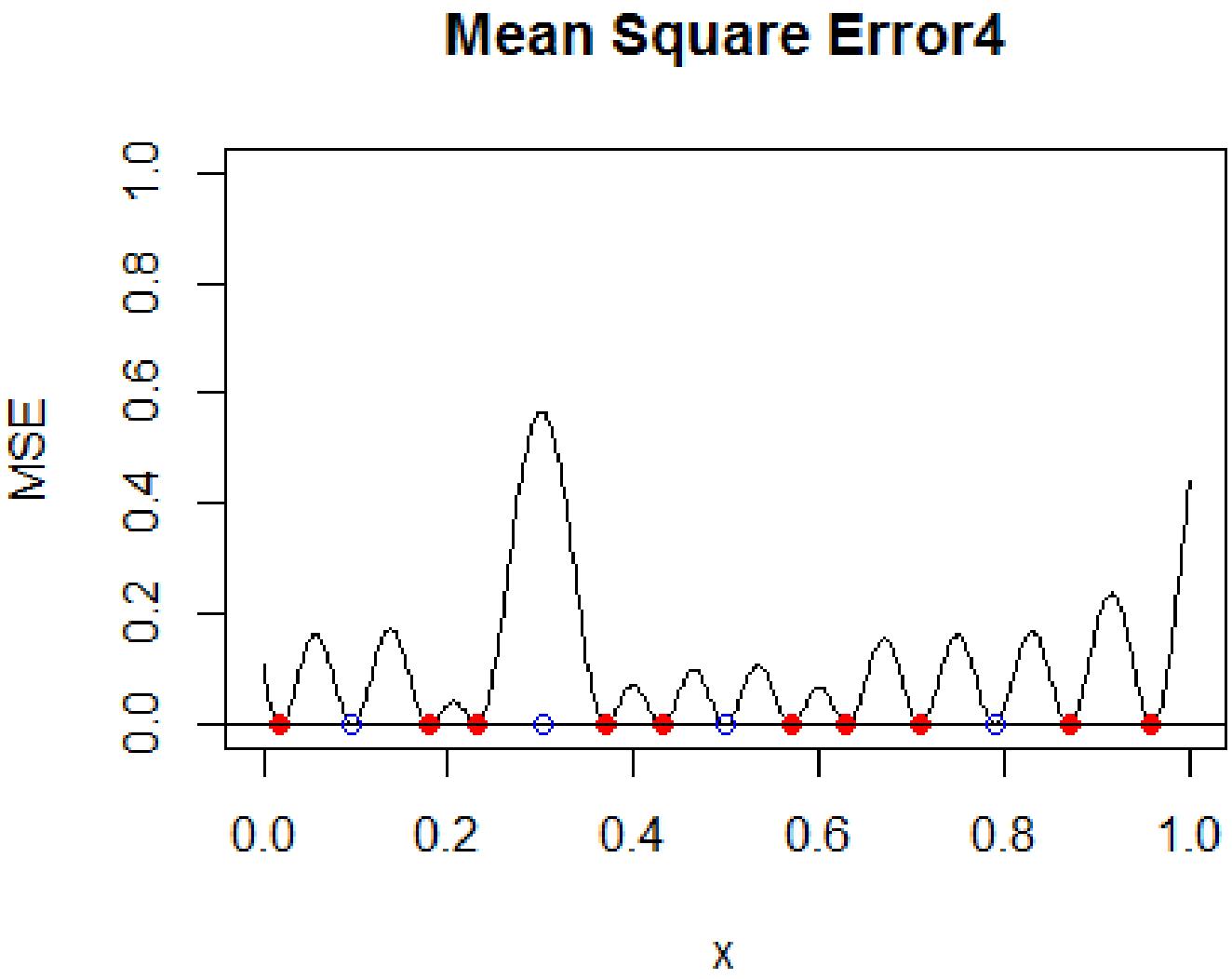

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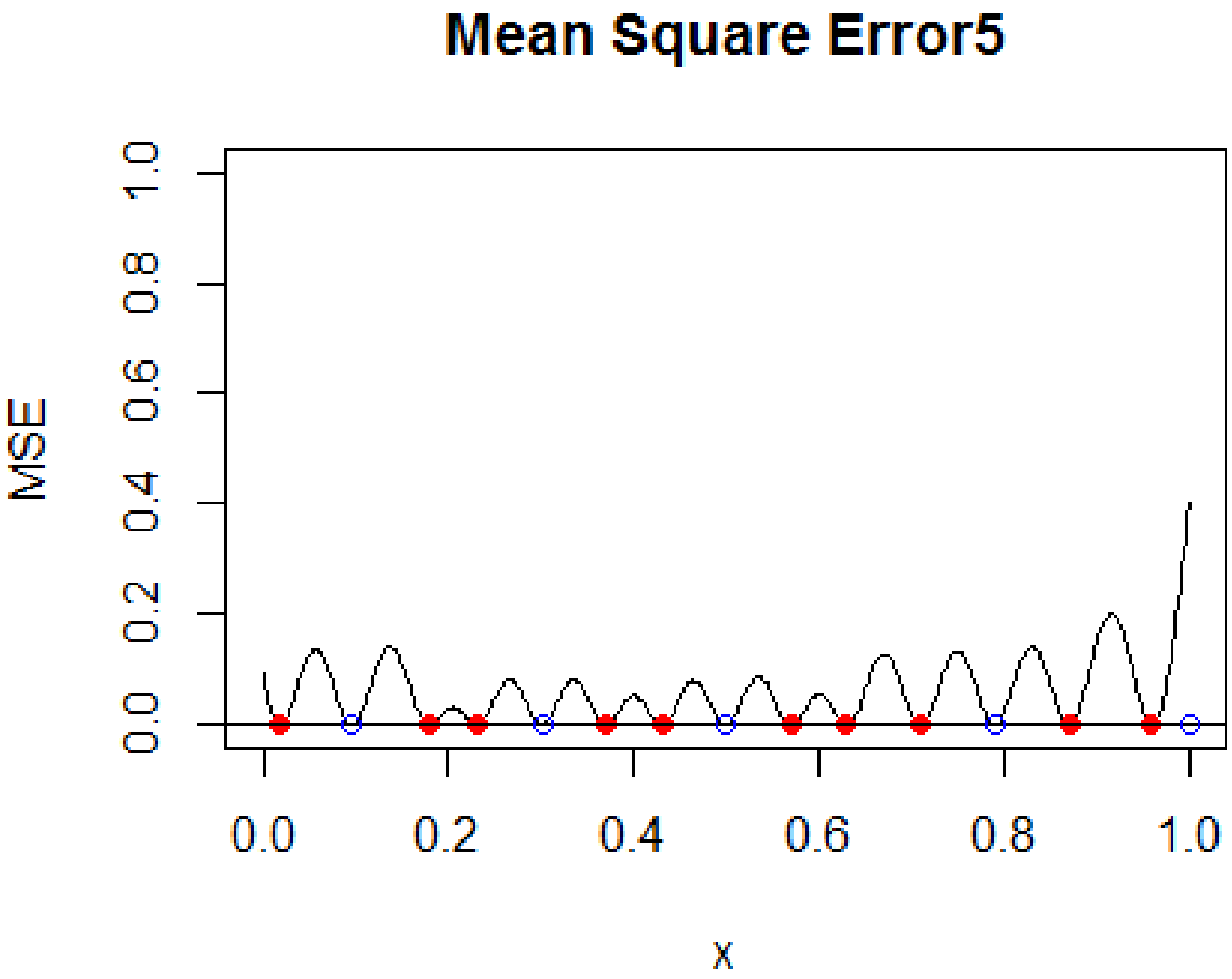

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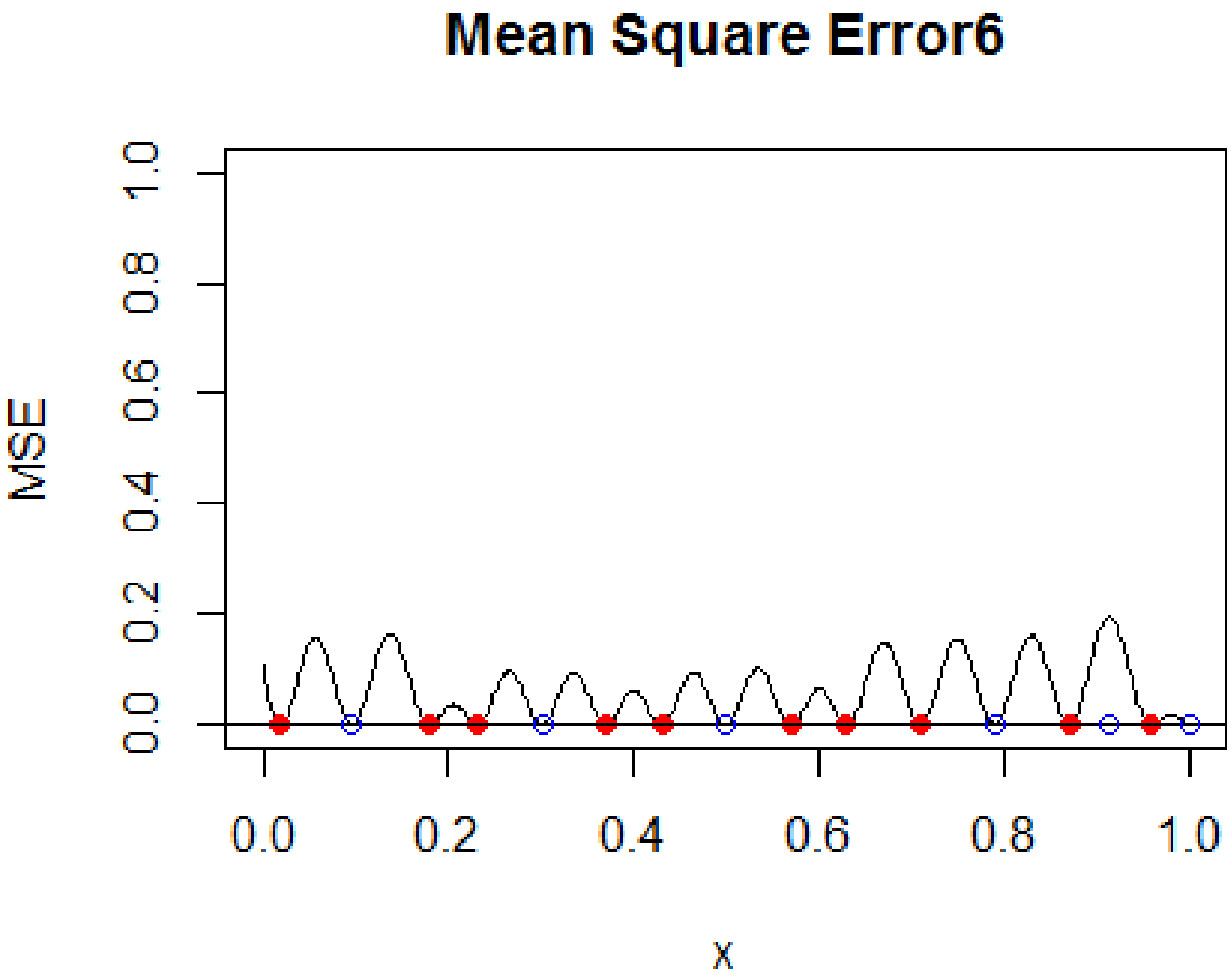

Illustration 1: Using meta-models for sequential design

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- Conclusions
  - Kriging
    - Uses Gaussian processes to interpolate a set of data points
    - Provides both a prediction and an estimate of the error of prediction over the entire domain
  - Advantages
    - Only needs a set of (experimental or numerical) data points
      - » Can be used if no model is available or with model-generated points
    - Easy to compute
      - » Provides a good approximation of the underlying process
    - Allows to define the locus of the next experiment that minimizes the highest uncertainty
      - » Model-free experimental design

Illustration 2: Prediction of runaway conditions

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- Industrial context
  - Some processes are highly exothermic
    - Oxidations, Fisher-Tropsch, Selective hydrogenations, …
  - Consequences of a thermal runaway are disastrous
    - Productivity loss, unit operability, material loss, environmental impact, human losses, ...
  - Importance for chemical companies
    - Ensure Safe Design
      - Determine a priori the safe and productive operating conditions
      - Justify alarm thresholds based on scientific criteria
      - Study transient phases: Start-up and shut-down procedures (programmed & emergency)

Illustration 2: Prediction of runaway conditions

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- Collaboration with Aix-Marseille University
  - To develop and evaluate tools to predict the evolution of unsteady state reactor behaviour
  - To apply the center manifold reduction methodology to an actual (semi-)industrial system

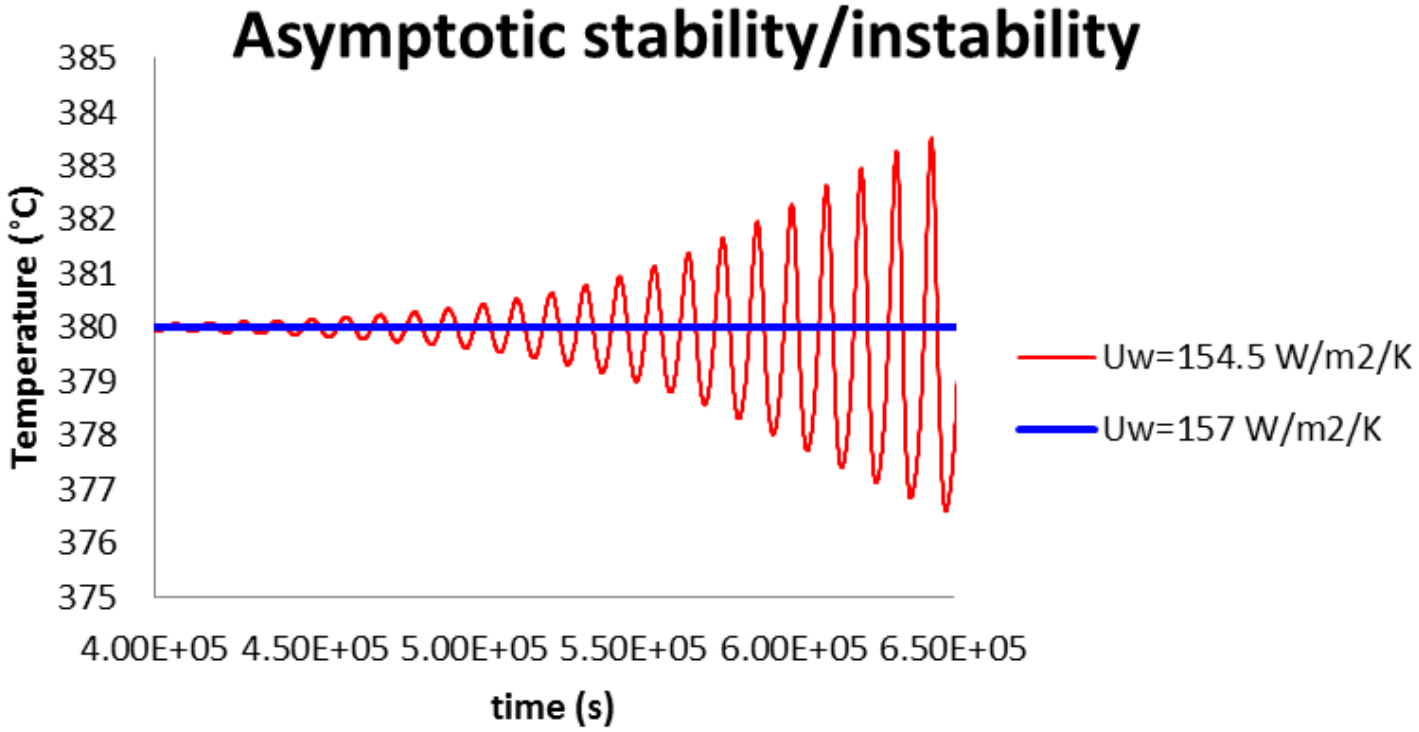

Illustration 2: Prediction of runaway conditions

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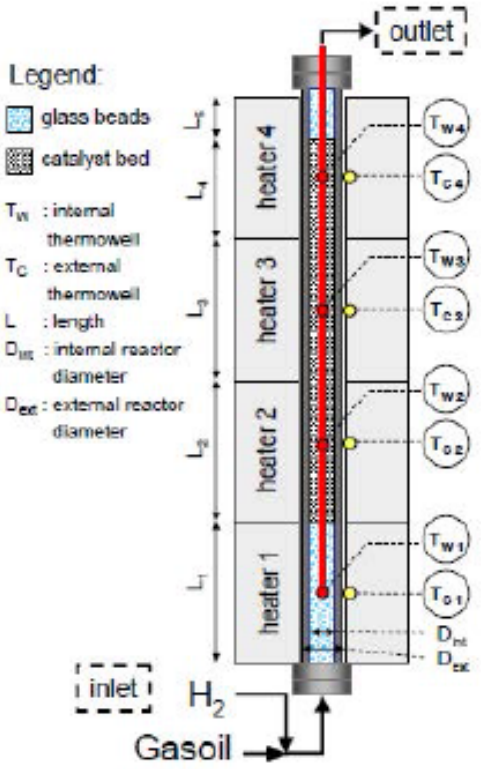
- Mathematical development at Aix-Marseille



Advection-diffusion-reaction system

$$\frac{\partial}{\partial t}\mathbf{V} = \frac{\partial}{\partial z}\mathbf{B}_a(\mathbf{V}) + \frac{\partial^2}{\partial z^2}\mathbf{B}_d(\mathbf{V}) + \mathbf{B}_r(\mathbf{V})$$

$\rightarrow$ Lumped families of chemical species, temperature, velocity

$$\mathbf{V} = (C_1^g, C_1^l, \cdots, C_m^g, C_m^l, T, u).$$

Discretization along the reactor axis z

$$\begin{aligned}\mathbf{y}(t) \quad = \quad & (C_1^l(z_1,t), \cdots, C_m^l(z_1,t), \cdots, C_1^l(z_{n_z},t), \cdots, C_m^l(z_{n_z},t), \\ & T(z_1,t), \cdots, T(z_{n_z},t))\end{aligned}$$

$\rightarrow$ Nonlinear dynamical system in $\mathbb{R}^n$ $(n = O(10^3))$

$$\frac{d}{dt}\mathbf{y} = \mathbf{f}(\mathbf{y}, \alpha)$$

Illustration 2: Prediction of runaway conditions

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- Mathematical development at Aix-Marseille

Theoretical framework

- Jacobian matrix $\mathbf{J}_0 = D\mathbf{f}(\mathbf{y}_0, \alpha_0)$, complex conjugate pair of eigenvalues (other eigenvalues stable) $\rightarrow \mathbf{J}_0\mathbf{v} = i\omega\mathbf{v}$, $\mathbf{J}_0\bar{\mathbf{v}} = -i\omega\bar{\mathbf{v}}$
- Parameter $\alpha = \alpha_0 + \beta$: state vector decomposition $\mathbf{y} = \mathbf{y}_s(\beta) + \mathbf{w} + \Psi(\mathbf{w}, \beta)$
- $\rightarrow \mathbf{w} = \tau(t)\mathbf{v} + \bar{\tau}(t)\bar{\mathbf{v}}$, the function $\Psi(\mathbf{w}, \beta)$ is the center manifold
- $\rightarrow$ for "sufficiently" small $|\beta|$ and $||\mathbf{w}||$

$$\frac{d}{dt}\mathbf{w} = \pi_0\mathbf{f}\left(\mathbf{y}_s(\beta) + \mathbf{w} + \Psi(\mathbf{w}, \beta), \beta\right) \quad \text{and} \quad \frac{d}{dt}\mathbf{y} = \mathbf{f}(\mathbf{y}, \alpha_0 + \beta)$$

are dynamically equivalent !

Aix-Marseille université irphé

Illustration 2:
Prediction of runaway conditions

- Limit Cycle Prediction

U_w = 155.2 W/m²/K

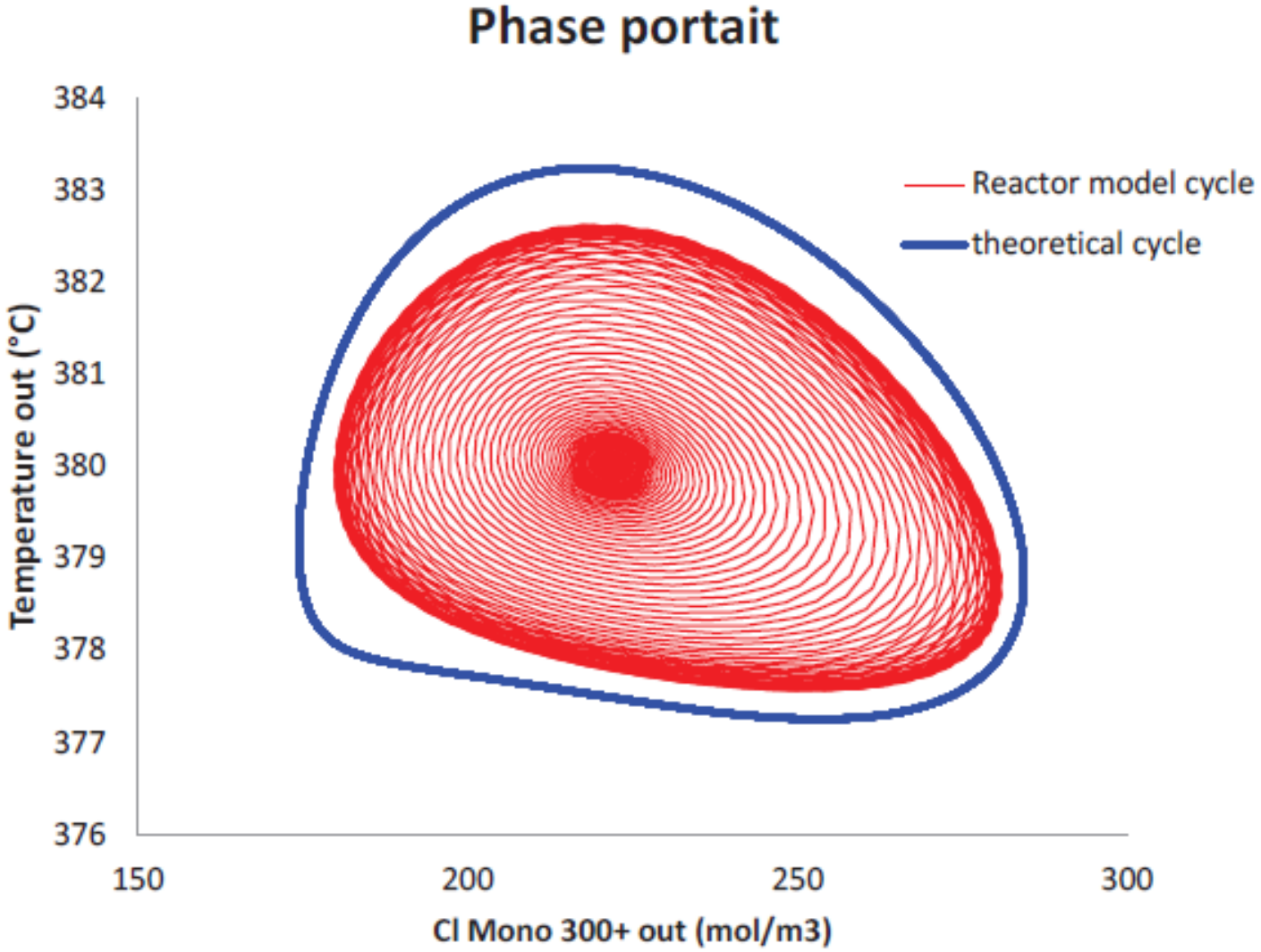

Illustration 2:
Prediction of runaway conditions

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- Limit Cycle Prediction

U_w = 154.5 W/m²/K

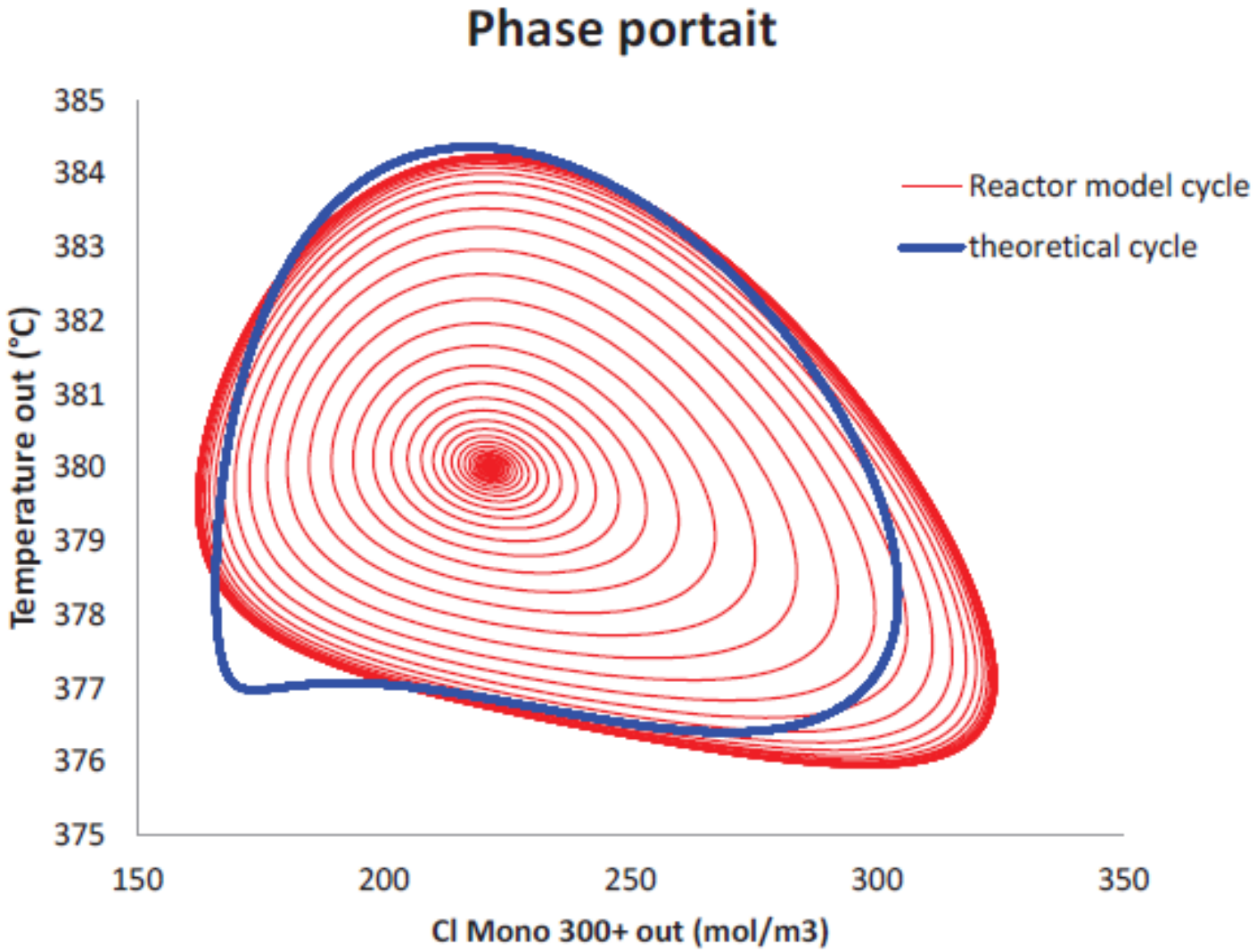

Illustration 2:
Prediction of runaway conditions

- Limit Cycle Prediction

U_w = 153.2 W/m²/K

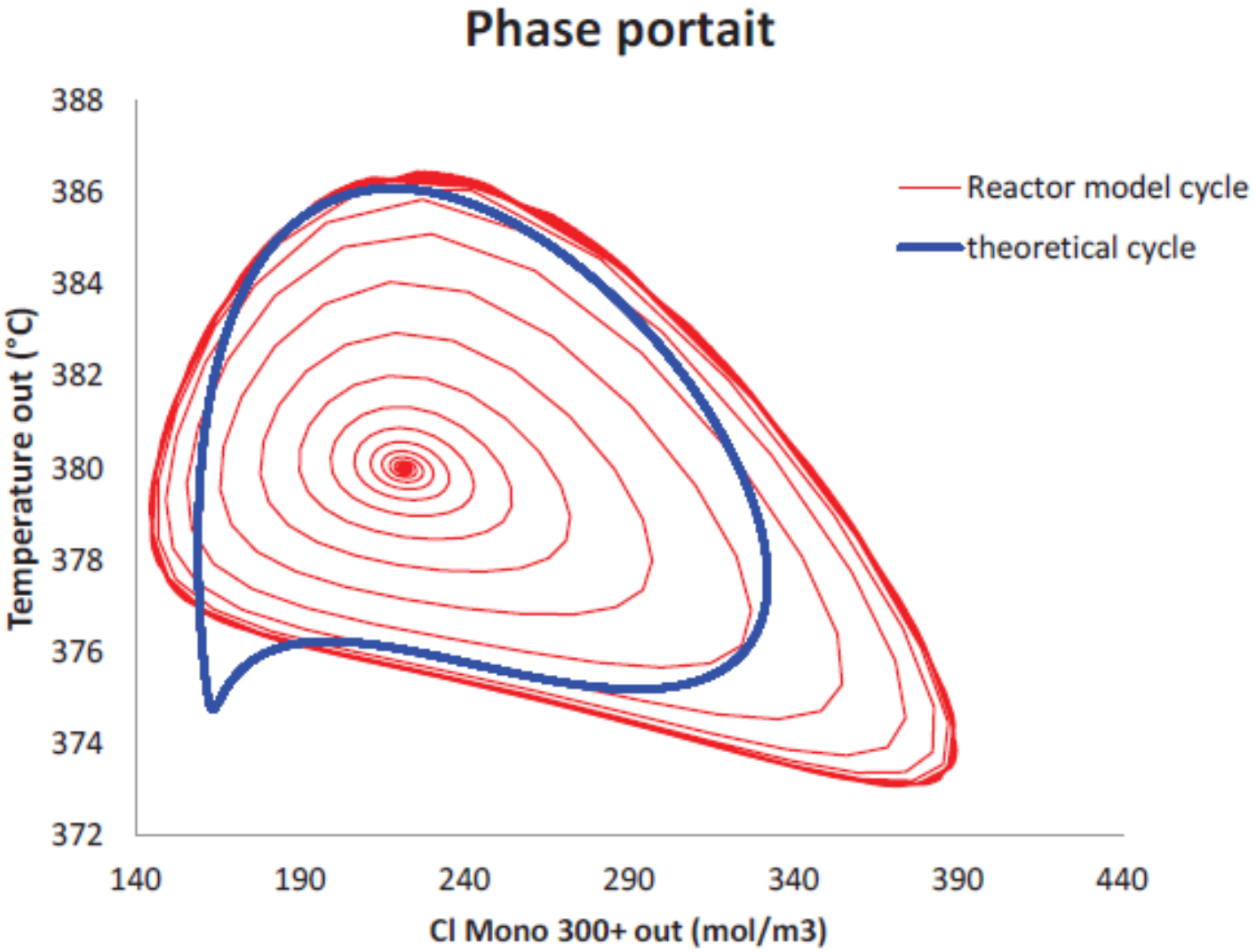

Illustration 2: Prediction of runaway conditions

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- Conclusions
  - Center manifold theorem
    - Analyzes the bifurcation of a dynamical system by projection onto a nonlinear amplitude equation
  - Numerical tool
    - Computer algebra capable of automatically performing the center manifold reduction process
  - Application to a chemical hydrotreating reactor model:
    - Numerically computed algebraic formula assesses the (local) existence of a limit cycle
    - Some extra-computation while numerically performing the stability analysis predicts the limit cycle
  - Valuable tool for full reactor systems with high sensitivity and slow transients

Conclusions

- Industry vs. Academia
  - Best practice in industry lags behind developments in academia
- Closing the gap: The Eurokin Consortium
  - Excellent exchange platform and network hub
    - Getting to know each other better
      - Industry needs vs. novel approaches
  - Delivers
    - High-level state-of-the-art reviews
    - Critical analysis of existing (experimental) tools
    - Easy-to-use tools


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Eurokin public website: http://www.eurokin.org